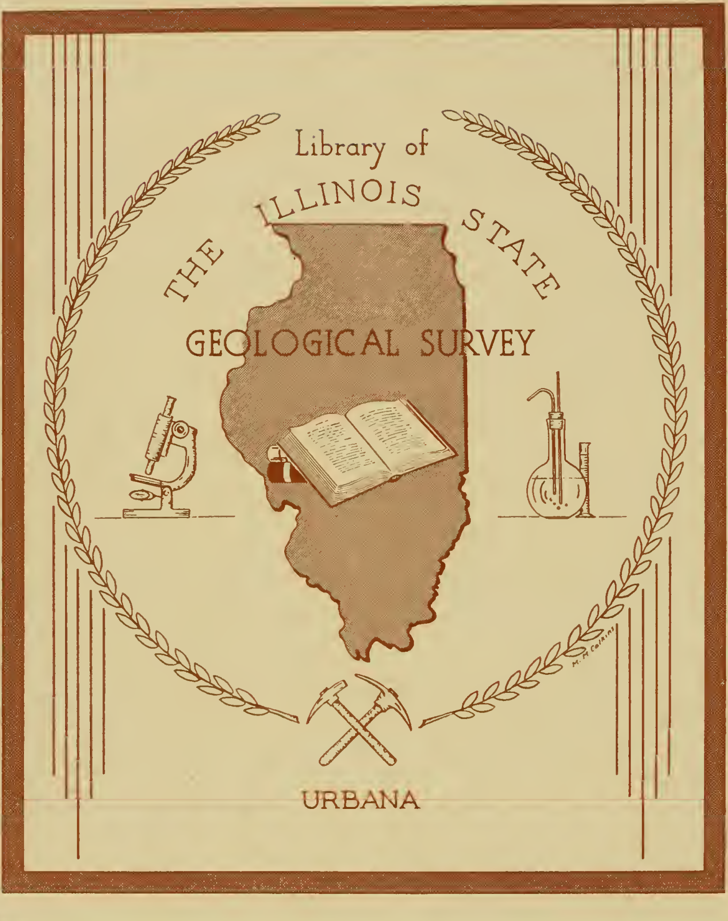

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CIRCULAR NO. 77

PREDICTING THE BEHAVIOR OF CLAY

BY

RALPH E. GRIM

REPRINTED FROM THE BRICK AND CLAY RECORD
VOL. 97. NO. 6. PP. 20-22, DECEMBER, 1940

AUG. 26TH 1818

PRINTED BY AUTHORITY OF THE STATE OF ILLINOIS

URBANA, ILLINOIS
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PREDICTING THE BEHAVIOR OF CLAY

WHY IS ONE SHALE PLASTIC, ANOTHER SHORT?

Research Work at Illinois Geological Survey
Explains Clay Mineralogy and Base-Exchange

Ralph E. Grim

It has been said with considerable accuracy that no two clays or shales have exactly the same properties. With equal accuracy it could be said that no one knows precisely why this is true. In other words no one knows "how" and "why" the properties of any clay or shale came to be as they are. To illustrate; why is one shale plastic, whereas another is short, even though it may look the same and may even show the same chemical analysis?

The answer to this question is a problem of research that is of primary interest to the ceramic industry. Obviously it will not be possible to control the properties of clays most advantageously and hence to utilize them to the best advantage until their properties are understood. Better manufacturing processes and better products await an understanding and, therefore, an improved control of clay properties.

Investigations through the years have gradually built up a fund of information regarding the properties of clays. Within recent years new approaches have been made to the problem and new ideas about the composition of clays have been developed which have greatly increased our understanding of the "how" and "why" of clay properties.

The use of X-ray diffraction analysis, improved microscopic technique, and thermal analytical methods in the study of clays have led to the so-called "clay mineral" concept of the composition of clays and shales. According to this concept most clays and shales are composed essentially of extremely small crystalline flake-shaped particles of one or more members of a small group of minerals known as clay minerals that have been given the names kaolinite, illite, and montmorillonite. In addition to the clay minerals, clays and shales may also contain varying amounts of certain so-called nonclay minerals such as quartz, limonite and feldspar. Organic material is also frequently present.

Clays and shales are made up of innumerable very small crystalline fragments having the form of a sheet of paper and being about 1/5,000 to 1/50,000 of an inch in diameter. Each minute sheet or flake is a particle of a clay mineral. Grains of quartz and other non-clay minerals of the same size or slightly larger than the clay minerals may be scattered through the clay mineral flakes. The nonclay mineral particles are in general granular and not flake-shaped. This is important because certain properties of clays, notably plasticity, are believed to be closely related to the presence of flake-shaped particles.

The properties of the three groups of clay minerals are not the same, and consequently two clays will not have the same properties if they are composed of different clay minerals. Stated another way, the properties of a clay will depend upon which clay mineral composes it. The following examples will bring out this point.

Kaolinite is white and fuses at high temperatures. Clays composed of kaolinite are characterized by relatively low shrinkage, medium to low plasticity, white to buff burning color, and high refractoriness. China clays, fire-clays, and some surface clays are examples of clays composed of kaolinite.

Montmorillonite is buff to yellow-green and fuses at relatively low temperatures. Clays composed of montmorillonite have the following characteristics: great plasticity, very high shrinkage, high bonding strength, red to brown burning color, and low fusion point. Montmorillonite clays disperse readily and thoroughly in water and under some conditions they form thixotropic suspensions. (Editor's Note: Thixotropy is the condition of a material which is somewhat rigid when undisturbed but which loses most of its rigidity upon agitation. Cup custard is a familiar example of a thixotropic suspension.) Bentonites and most fuller's earths are composed of montmorillonite. Montmorillonite is also a component, with other clay minerals, in many surface clays and some kaolins and shales. One of the outstanding attributes of montmorillonite is that its effects on the properties of a clay are out of all proportion to the amount actually present. Thus, one per cent or so in a clay may exert a very large influence on the properties of the clay.

Illite is usually yellow-green. Clays and shales composed of illite are not refractory and almost always have a red burning color. The plastic properties vary; thus some illite materials have high plasticity, high shrinkage, and high bonding strength, whereas others have low plasticity, low shrinkage, and low bonding strength. Illite is the dominant component of many shales. It is also one of the constituents of many fire-clays and surface clays.

From a chemical standpoint all of the clay minerals are compounds of alumina, silica and water. Montmorillonite may also contain iron, alkali earths such as magnesia, and alkalies such as soda. Illite contains potash and may also have iron and magnesia. A chemical analysis of a clay does not always disclose the identity of the clay mineral composing it. Everyone familiar with clays is aware of the fact that two clays with vastly different properties may yield the same chemical analyses. On the basis of the clay mineral concept this is readily explained by the presence of different clay minerals in the two clays. Stated another way, the properties of a clay are not determined so much by the amount of silica, alumina, etc., that it contains as by the manner of the occurrence of the silica, alumina, etc., in kaolinite, montmorillonite, or illite. If the alumina and silica are present in the form of montmorillonite, the clay will have one set of properties; if they are present in the form of kaolinite, it will have another set of properties.

QUARTZ GRAINS IMPORTANT

This does not mean that clay mineral composition is the only factor that controls clay properties. Other factors are important also. Thus, two clays of the same clay mineral composition will have different properties if one has no quartz and the other contains an appreciable amount of quartz. Not only the amount but the size of the quartz grains is important. An example is the famous Gros Almerode glass pot clay which is very plastic, even though it contains about 50 per cent quartz. Usually this amount of quartz will cause a clay to be short, but in this particular case the quartz is so fine grained that the plasticity remains high. Because of the large amount of quartz the shrinkage is very low. Organic matter may also be important. In fact, many ball clays owe a considerable amount of their plasticity to their content of organic material.

Recent researches are attempting to go beyond the mere determination of the clay mineral composition and learn why it is that the individual clay minerals provide the properties they do. Why, for example, does montmorillonite have higher plastic properties than kaolinite? Studies of the atomic structure of the clay minerals are beginning to answer such questions. At the present time there are reasonably satisfactory concepts of the arrangement of the silicon, aluminum, oxygen, and other atoms in the clay minerals based on X-ray analyses. On the basis of these concepts, it has been possible, perhaps for the first time, to begin to get a clear insight into the mechanism of plasticity, bonding power, etc. This is an interesting story that warrants separate treatment.

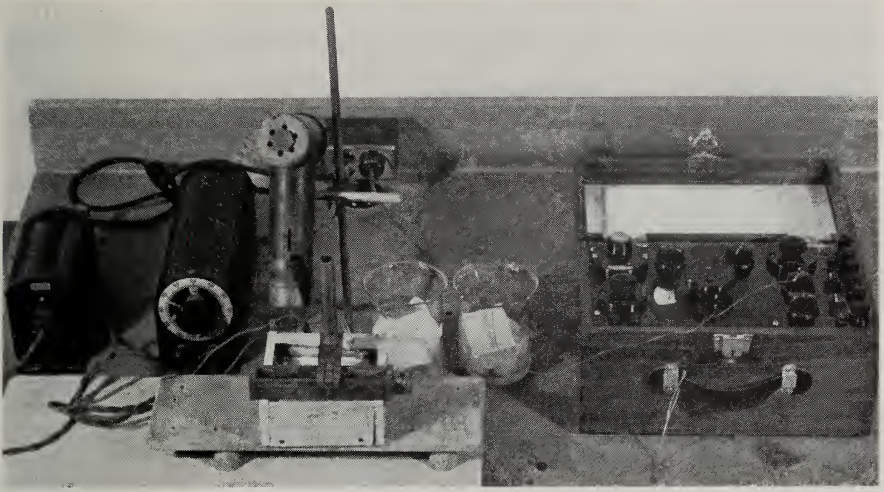

Fig. 1.—Apparatus for identifying clay minerals by determining their optical characteristics at temperatures up to 200° C. It is essentially a rather novel refractometer built in a small furnace. The potentiometer on the right is for temperature determinations.

The question may well be raised—what practical value do such researches have? Several of many possible illustrations will perhaps best answer this question. It is a well known fact that certain shales laminate badly when they are extruded, whereas others show only a small amount of lamination. Research showed that characteristics of certain clay minerals favor the development of lamination. Consequently before a shale is run through an extrusion machine, it is now possible to predict how badly it will laminate. If a plant is stuck with a shale that laminates badly, it is frequently possible to recommend certain steps that can be taken to reduce the amount of lamination.

Blend Clays

Usually a given clay or shale bank does not contain entirely uniform material throughout. There is, therefore, the frequently neglected opportunity to improve the raw material by selective mining or by blending material from various parts of the bank in definite proportions. Obviously such selective mining or blending can be done only on a hit or miss plan if the materials are not thoroughly understood. Many a plant could make better ware more economically if the available raw materials were well understood.

An investigation by the Illinois State Geological Survey of the clay in the pit of an Illinois producer revealed that a bed of clay previously discarded as worthless possessed valuable properties for certain uses outside the field of ceramics. This clay, for years considered a waste material, is now extremely valuable material.

Numerous other examples could be

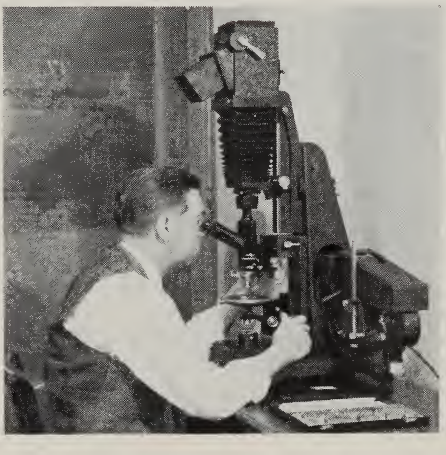

Fig. 2.—Microscope for studying thin sections and powders of minerals with magnifications of the order of 1,500 to 2,000 diameters. On the right may be seen the housing of a brilliant arc lamp and at the top is a camera attachment.

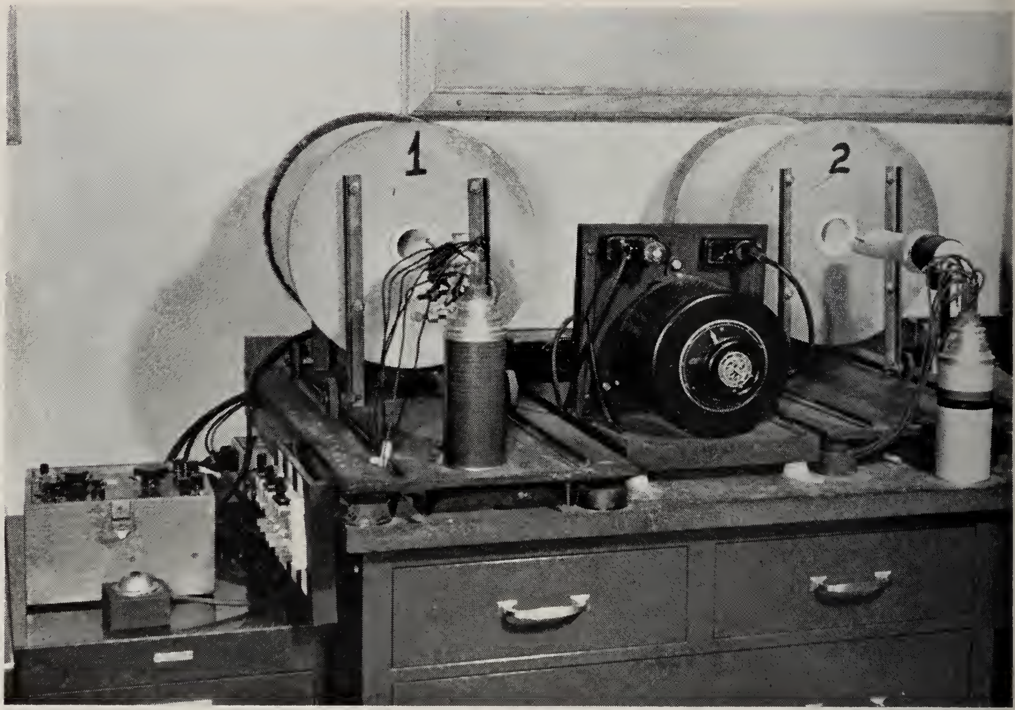

FIG. 3—Equipment for making differential thermal analyses of clays.

given from the files of the Illinois State Geological Survey. This Survey has gradually built up a huge fund of information on the composition and properties of the clays in Illinois. These data are available free of charge to the industry in the State, and they have been of great value in expanding and improving products and in solving processing problems.

It has been known by clay men for a long time that the addition of certain salts, acids, and alkalies to clays cause a change in their properties. Experiments and experience have shown that not all clays are affected the same way by the same electrolytes—in fact the same chemical added to two clays might cause a beneficial change in one and a detrimental change in the other.

In the last few years the chemical treatment of clays, sometimes with attempted control by means of pH measurements, has become a fad. Nevertheless the fact remains that there has been little understanding of "how" and "why" electrolytes affect clays. Recent researches on the subject of base-exchange are rapidly throwing light on this problem.

BASE-EXCHANGE EXPLAINED

The phenomenon of base-exchange can be best understood by analogy with permutite or zeolite water softeners. The presence of lime in water is usually what makes it hard. It is softened in the permutite or zeolite softeners by substituting soda for the lime. In this process the hard water is percolated through a mineral material (the zeolite) which contains soda. As the water percolates through the zeolite, the lime goes from the water to the zeolite in exchange for the soda which goes from the zeolite to the water. In the exchange the structure of the zeolite is not altered. The process can be reversed by passing a strong salt solution through the zeolite, in which case soda will go from the solution to the zeolite in exchange for lime.

The clay minerals have this same property of carrying basic ions, which,

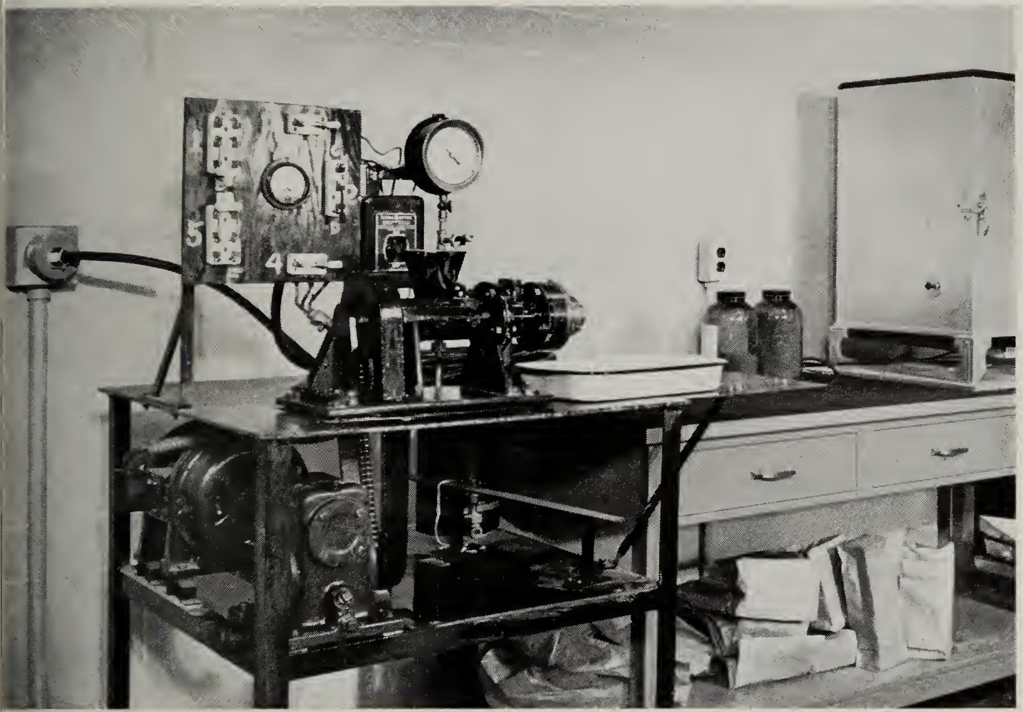

Fig. 4.—Apparatus for studying the forming of clay bodies by Extrusion.

under certain conditions, are exchangeable for other ions, without changing the structure of the clay minerals. The capacity for base-exchange is greatest for montmorillonite and least for kaolinite. It is generally believed that the exchangeable ions are held on the surface of the clay mineral particles.

Of great significance is the fact that the properties of clays vary according to the identity of the exchangeable base present. For example, two clays composed of montmorillonite and identical in every way, except that one carries sodium as the exchangeable base and the other carries hydrogen, will have different properties. The sodium clay will swell in water, easily form a thick suspension, and have extremely high drying shrinkage. The hydrogen clay will swell a negligible amount, form a suspension with difficulty, and have lower shrinkage.

The far reaching commercial possibilities of using the base-exchange property of clays are obvious. It should be possible to treat many clays (those with clay minerals of reasonably high base-exchange capacity) with the proper ion to get the properties most desired. Researches are going forward in several laboratories to determine precisely the effect of various exchangeable bases on clay properties. The Illinois State Geological Survey has undertaken an investigation of the exact influence of the common basic ions on the ceramic properties of the pure clay minerals. It was felt that such fundamental data had to precede the study of base-exchange in raw clays, many of which are mixtures of various clay minerals.

Recent base-exchange clay researches have the further advantage of enhancing greatly our concept of the mechanism of plasticity, bonding power, etc., in clays.

Although electrolyte treatment of clays is closely related to the base-exchange phenomenon, it cannot be concluded that this is the only means whereby electrolytes affect the properties of clays. There is good reason to believe that when certain chemicals are added to a clay they act as cementitious agents or react chemically with the clay to form new compounds that have cementitious properties.

To summarize, recent clay mineral and base-exchange researches are throwing much light on the ''how'' and ''why'' of the properties of clays and hence are directing the way to the more economical production of a larger number of better clay products.

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